CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Superabsorbent polymers (SAPs)

The materials that their absorbing capacity is greater than 15 times their own weight in the aqueous fluids such as water, electrolyte solution, including synthetic urine, brines, and biological fluids such as urine sweat, and blood have so many called names as superabsorbent polymers (SAPs), or hydrogel, or water containing gels, or highly water absorbing polymers (HWAPs), etc. Not only they are of high fluid absorbing capacity, but the absorbed fluid is hard to release also, as they merely immobilize the fluid by entrapment rather than by holding it in the structure [6]. They are polymers which characterized by hydrophilicity, insolubility in water [7], and cross-linked polyelectrolyte. Because of their ionic nature and interconnected structure, they absorb large quantities of water and other aqueous without dissolving [8].

Many kinds of SAPs have been commercialized since the hydrolyzed starch-polyacrylonitrile graft copolymer; the superslurper was first developed by the Northern Regional Laboratory of the United States Department of Agriculture in the early 1970's. They are widely applied not only in the fields of personal care products, biosorbent, bio-material, but also in agriculture and industrial applications, and for many of them, dealing with leaking water is also a common theme. For example, leaking water is often a problem in the construction industry. One new product is a sealing composite that swells slightly in water. It is made by blending superabsorbent powder into rubber with the aid of a surfactant-like substance [4]. Leaking water can also degrade the performances of fiber optic communication cables and power

transmission cables [9]. Water blocking tapes, made by applying a superabsorbent polymer and a polymeric binder onto non-woven fabric were wrapped around the cable, beneath the plastic covering, and intercept water that gets through them [10].

In addition to their liquid-water absorption characteristic, superabsorbent can absorb and release moisture from the air more effectively than silica gel. This property can be used to prevent damage due to moisture condensing on walls and ceilings in humid buildings, help maintain a constant humidity in vegetable and fruit storage buildings, and prevent spotting of the produce caused by water dripping from the surface of the structure. They have been developed to be superabsorbent sheets or superabsorbent fiber. Not only that but they can also help conserve water in agriculture and horticulture and improve the air content of the clay soil [4].

As mentioned above, SAPs have been mainly used and developed only in the limited field of disposable absorbing materials such as diaper and sanitary napkins, recent their applications are being extended into others industrial are as [6]:

1. Disposable absorbing materials:

   - Sanitary napkins

   - Diapers for infants & adults

   - Medical sheets

   - Paper towel & non woven, sheets

2. Agriculture & horticulture:

   - Soil conditioners for water retention

   - Coatings for seed germination

- Hydro-mulching formulations

3. Industries:

- Dehydrating agents for fuels

- Blocking agents for underground cables

- Sludge dewatering

- Sealing gaskets

4. Others:

- Swellable toys

- Fire fighting fluids

- Wallpapers for humidity control

- Ice pack

- Debris flow control [4]

- Artificial snow [4]

- Gel actuators [4]

- Matrices for controlled release devices [11]

Generally, SAPs are classified into the four categories as [6]:

1. By raw materials

   a) Starch grafts, carboxymethylated

   b) Cellulose graft, carboxymethylated

   c) Synthetic polymer: poly(acrylic acid), poly(vinyl alcohol), poly(oxymethylene)

2. By method on insolubilization

   a) Graft polymerization

   b) Chemical crosslinking

   c) Self-crosslinking

   d) Radiation crosslinking

   e) Introduction of crystalline structure or hydrophobic groups

3. By method of hydrophilization

   a) Polymerization of hydrophilic monomers

   b) Carboxymethylation of hydrophilic polymers

   c) Graft copolymerization of hydrophilic polymer on hydrophobic polymer backbone

   d) Hydrolysis of nitrile groups and ester groups

4. By Product Form

  a) Powder

  b) Film

  c) Fiber

By the raw materials, SAPs are divided into starch and cellulose-based polymers and synthetic polymers. The physical properties of SAPs are dependent upon the methods of insolubilization and hydrophilization introduced into the SAPs and upon the appearance of products in powder, film, and fiber.

Because SAPs belong to a group of hydrogel, which can be further classified as [12]:

  1. By hydrogels' charge

  a) Neutral hydrogels

  b) Anionic hydrogels

  c) Cationic hydrogels

  d) Ampholytic hydrogels

  2. By method of preparation

  a) Homopolymer networks

  b) Copolymer networks

  c) Multi-polymer networks

d) Interpenetrating polymeric networks

3. By physical structural features of the system

   a) Amorphous hydrogels

   b) Semi-crystalline hydrogels

   c) Hydrogen-bonded structures

   d) Super-molecular networks structures

   e) Hydro colloidal aggregates

4. By their mechanical and structural characteristics

   a) Affined networks

   b) Phantom networks

In general, water-soluble monomers include ethylenically unsaturated amides such as acrylamide, methacrylamide, and fumramide as well as their N-substituted derivatives. Ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, and crotonic acids and their salts are preferred. Suitable poly(carboxylic acids) includes maleic acid, fumaric acids, and itaconic acid. Preferred ethylenically unsaturated carboxylic acid esters include hydroxyethylacrylate, hydroxyethylmethacrylate, and esters of acrylic and methacrylic acids with poly(ethylene oxide). Vinyl amines such as vinyl pyridine and vinyl morpholine, and diallyl amines are also useful.

The monomer mixture typically includes one or more cross-linking monomers which comprises organic compound having two or more ethylenic groups

copolymerizable with the water-soluble monomers of the monomer mixture. For example, cross-linking monomers include diacrylate or dimethacrylate of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, neopentyl glycol, trimethylol propane and pentaerythritol, triacylates or tetramethacrylate of pentaerythritol, *N,N'*–methylenebisacrylamide, *N,N'*–methylenebismethacrylamide, and triallyl isocyanurate. Preferred cross-linkers include methylenebisacrylamide, trimethylol propanetriacrylate and diethylene glycol diacrylate and tetraethylene glycol diacrylate [13].

2.1.1 General properties of superabsorbent polymers

As mentioned above superabsorbent polymer can absorb water up to several thousand times its own weight and keep this water under pressure. The absorbed water can be released slowly when the SAP is put in dry air to maintain the moisture of the environment. Most SAPs are in principle crosslinked hydrophilic polymers [5].

Because of these unique properties, SAPs have many novel potential applications in various areas. For example, they can be used in baby diapers, sanitary towels, athletic garments, as carriers of contamination prevention agent, used as ship bottom paints to prevent the formation of microorganism, adhesives and food packing, etc. In agriculture and horticulture, it is being used as a plant growth medium to improve the water retaining property of sandy soil, in civil engineering as a friction reducing material for placing pipe for sewage transport, in environmental protection, as a sludge dehydrating treatment agent for solidifying waste and to absorb heavy metal ions such as Cr^{3+} and Co^{2+}.

There are many methods to prepare SAP from various staring materials, such as copolymerizing the hydrophilic monomer with a cross-linking agent, grafting monomers with starch, cellulose, synthetic fiber, and polysaccharide, crosslinking linear hydrophilic polymer with polyvalent metal ions or organic multifunctional group materials etc. The product of SAP can be in the form of small particles, powder, fiber, membrane, micro beads and even liquid.

The SAPs can be classified with different methods. From a morphological point of view, they can be divided into particle, powder, spherical, fiber, membrane and emulsion types etc. The morphology of SAP is designed to respond the different requirements of the applications. For example, the powder product can be put in the multilayer sheet to form sanitary napkin and diapers, the particle and spherical product can be used as deodorant, the fiber product can be used as antistatic electric fiber, the membrane product can be used as antifost sheet while the emulsion product can be used in soaking and painting.

Water absorption capacity (WAC) is the most important characteristic of superabsorbent polymer. There are many ways to measure WAC, however, there is no standard yet. Usually, the WAC is measured using the volumetric method, gravimetric method, spectroscopic method and microwave method. The volumetric method is to measure the volume changes of polymer (or the water) before and after the absorption, the gravimetric method is to measure the weight changes of polymer, the spectrometric method is to measure the changes in the UV-spectrum of the polymer and the microwave method is to measure the microwave absorption by energy changes.

The water absorption capacity (WAC) of the SAPs depends upon its composition and structure generated from the preparation method, as well as the presence of electrolytes in the water. For example, the WAC of SAP can be thousand

gram water per gram SAP when in contact with pure water, but when it is put into water containing urine, blood and metal ions, the WAC will be reduced to only one tenths of its maximum value.

Superabsorbent polymers are crosslinked network of flexible polymer chain. The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups. The factors that supply absorbing power to polymers are osmotic pressure based on movable counter-ions, and affinity between the polymer electrolyte and water. The factor that suppresses absorbing power, in contrast, is found in the elasticity of the gel resulting from its network structure. The absorption mechanism before and after swelling in a dilute salt solution of an example of a superabsorptive resin, in the case of a crosslinked polymer with sodium carboxylate groups is shown in Figure 2.1

Before absorption, long chains of polymers are interwoven, and polymers make a three-dimensional structure by crosslinking between the chains to make a dense phase. These SAPs instantaneously absorb water and swell with dissolution of Na^+, owing to the hydrophilic ionic groups, and becoming a gel [14].
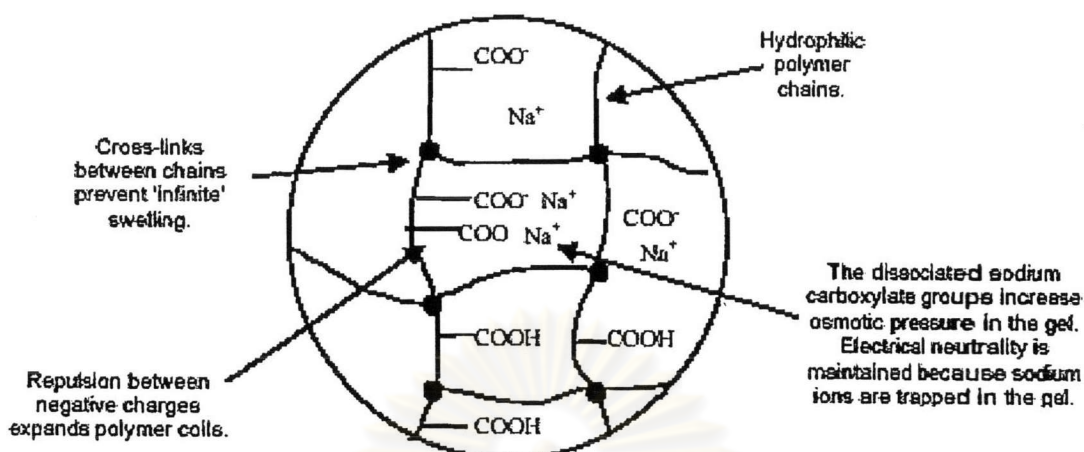
Figure 2.1 Mechanism of swelling of superabsorbent polymers

During absorption, water moves into a particle of superabsorbent polymer because the activity of water is initially lower in the interior of the particle. As water diffuses into the particle, the particle volume increases and the polymer chains that form the superabsorbent polymer network must also move generally in a direction opposite to that of the water molecules, in order to accommodate the volume of the additional molecules of water. After absorption, the change in volume is observed because polymer molecules are much larger than water molecules, they diffuse much more slowly. Not only are the polymer molecules larger, but they are also connected one to the other by the crosslinks, that the polymer does not eventually dissolve in the water and become useful as a superabsorbent.

Therefore, the absorbency is mainly dependent upon three factors [6]:

a) the osmotic pressure

b) the molecular chain expansion resulting from electrical repulsion between the electrolyte anions in the polymer chains

c)   the extent of cross-linkage affecting the degree of swelling of polymer.

The water absorbency (Q) can be expressed by the Flory's equation [6] shown below.

$$Q^{5/3} = [(I / 2V_uS*^{1/2})^2 + (1/2 \bar{\chi_1})/V_1)(\upsilon_0/V_0)$$
2.1

where,

I = degree of ionization of polymer electrolyte

$S*$ = ionic strength of salt solution added

$(1/2- \chi_1)/V_1)$ = affinity between ionic network and the absorbed water

V_u = molar volume of polymer repeating unit

υ_0/V_0 = crosslinking density

The important physical properties of absorbent polymers depend on the precise structure of the polymer network. The key importances for use in personal care applications are the equilibrium swelling capacity, the rate of swelling and the modulus of the swollen gel. These properties of the product both are related to the cross-link density of the network: modulus increases and swelling capacity decrease with increase cross-link density [12].

2.1.2 Applications of superabsorbent polymers

Superabsorbent polymers possess a number of attributes that make them very attractive in many different applications. Superabsorbent polymers have supplanted much of the traditional absorbents in infant diapers and have made significant improvements in the performance of feminine hygiene products and adult incontinence products as a result of superior water-absorbing properties. The basic property of water absorption has suggested the use of superabsorbent polymers in many other applications, including paper towels, surgical sponges, meat trays, disposable mats for outside doorways and in bathrooms, and for household pet litter, bandages and wound dressings. The ability of the swollen gels to release the water to the surroundings as vapor has also been used in various ways, for example, as humidity-controlling products or as soil conditioners. Superabsorbent polymers may also be used to release water-soluble substances from within the network structure into the surrounding as a solution. For example, pharmaceuticals and fertilizers may be incorporated into superabsorbent polymer to yield controlled release products.

Another characteristic of the swollen polymer is its rubbery nature, which has been used to control the consistency of products as diverse as cosmetics or concrete or to contribute a soft, yet dry, feel to a product like a hot or cold pack for sore muscles. The soft, rubbery nature may also be employed to impart sealing properties to products that are in contact with water or aqueous solutions, for example, underground wires and cables [15].

2.2 Superabsorbent polymer composites

2.2.1 Intercalation mechanism

SAP composites (SAPC) is prepared by intercalating a monomer into the interlayer space of sheet silicates. Typical silicates are montmorillonite, zeolite, talc, Li-montmorillonite, vermiculite etc. The most applicable silicate is three-layer (2:1) clay minerals. The basic structure unit is composed of an aluminum oxide (octahedral) layer between two silicon oxide (tetrahedral) layer such as montmorillonite In the interlayer space, there are exchangeable cations such as Na^+, Ca^{2+}, Mg^{2+} etc, which can exchange with inorganic metal ions, organic cationic surfactant and cationic dyes [5].

Whether the intercalation and the associated planner expansion can proceed or not mainly depends upon the reaction free enthalpy (ΔG). If the $\Delta G < 0$, this process can go spontaneously. For an isothermal process, $\Delta G = \Delta H - T\Delta S$, $\Delta G < 0$, $\Delta H < T\Delta S$ is required. To meet the above condition, there are two processes in three ways

Exothermal process: $\Delta H < 0$, and $\Delta S > 0$,

$$\Delta H < T\Delta S < 0$$

Endothermal process: $0 < \Delta H < T\Delta S$.

The ΔH term is mainly composed of the strength of the interaction between the monomer or polymer molecule and the clay, and the polymerization enthalpy of monomers in the interlayer of clay. The entropy change (ΔS) is related to the restricted state of solvent, monomer and polymer molecules, and the entropy of polymerization of the monomer in the layer.

According to the combination process, the intercalation can be divided into two types. 1. monomer intercalation and *in situ* polymerization: disperse the monomer,

intercalate it into the silicate interlayer space, and execute the polymerization: 2. polymer intercalation: mix the melted or dissolved polymer with the silicate by a mechano-chemical or thermo-dynamic chemical function to finish the intercalation process. As a practical method, this can be further divided into (i) solution method and (ii) melting method. By combining with the above routes, four practical processes are generated: 1. melting intercalation of polymer, 2. solution intercalation of polymer, 3. melting intercalation and subsequent polymerization of the monomer, and 4. solution intercalation and polymerization of monomer.

There are three kinds of states in the composite structure as shown in Figure 2.2. First, AM intercalated into the interlayer space of inorganic component is weakly bound by Van der Waals forces and hydrogen bonds to the hydrated interlayer cations and the silicate layer, respectively (Figure 2.2, A-sites). Secondly, AM is bound to the inorganic component surface by hydrogen bonds with exchangeable surface cations in the structure of inorganic component (Figure 2.2, B-sites).

Finally, a free polymer network is formed between inorganic component particles (Figure 2.2, C-sites) that link the inorganic component plates to each other via polymer strands. Because initially AM exists at all three bonding sites in the sample, on exposure to ionizing radiation simultaneous polymerization occurs. Therefore, the overall structure of the composites will be quite complex. It is our current understanding that it is this complex structure that imparts the composites material better performance in terms of water absorption capability and thermal stability when comparing to the material that had only the intercalated polymer at A-sites.
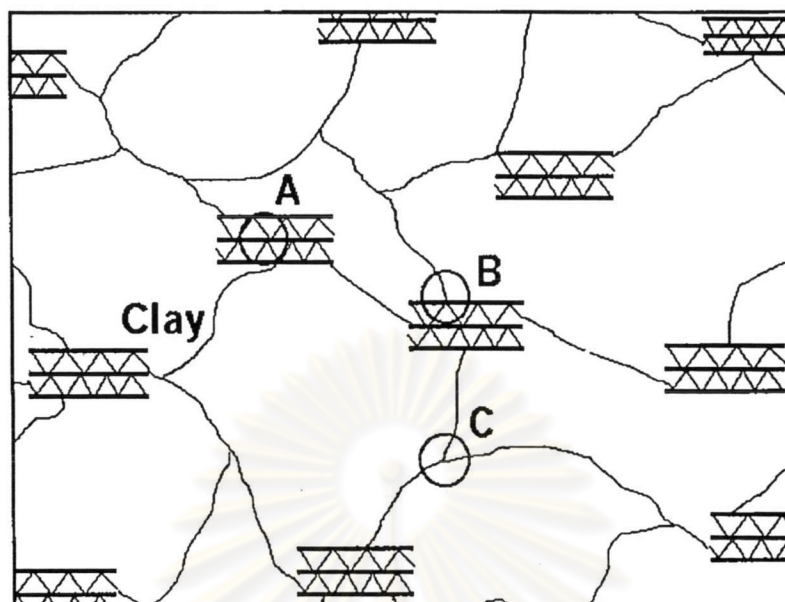
A site: polymer intercalated into the lamina of inorganic component

B site: polymer attached to the surface of inorganic component particle

C site: free polymer network

Figure 2.2 Schematic structure of superabsorbent polymer composites

## 2.3 Mechanism for free radical copolymerization

The structure of the polymeric network is ultimately determined by the method of synthesis. One of the most important types of addition polymerization is initiated by the action of free radicals, electrically neutral species with an unshared electron. All free radical addition (chain growth) polymerizations have at least three basic reaction types occurring simultaneously during polymerization. These include: initiation reactions that continuously generate radicals; propagation reactions that are responsible for the growth of polymer chains by monomer addition to a radical center; and termination reactions between two radical centers that give a net consumption of radicals [16]. Free radicals for the initiation of addition polymerization are usually generated by the thermal decomposition of organic peroxides or azo compounds. The

initiator molecule, represented by I, undergoes a first-order decomposition with a rate constant k_d to give two free radicals, $R^{\cdot}$:

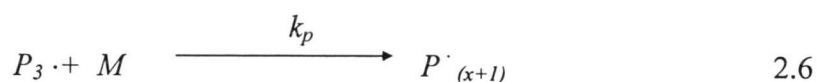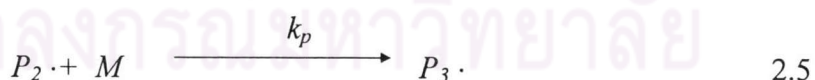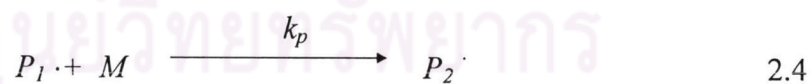$$I \xrightarrow{k_d} 2\,R^{\cdot} \qquad\qquad 2.2$$

The radical then adds a monomer by grabbing an electron from the electron-rich double bond, forming a single bond with the monomer, but leaving an unshared electron at the other end:

where $P_1^{\cdot}$ represents a growing polymer chain with 1 repeating unit

$$R^{\cdot} + M \xrightarrow{k_i} P_1^{\cdot} \qquad\qquad 2.3$$
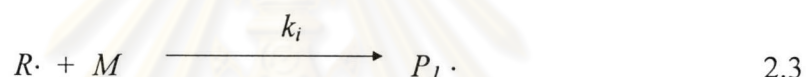
In practice, not all the radicals generated in reaction 2.2 actually initiate chain growth as in reaction 2.3. Some recombine or are used up by side reactions.

The product of the addition reaction is still a free radical; it proceeds to propagate the chain by adding another monomer unit:

$$P_1^{\cdot} + M \xrightarrow{k_p} P_2^{\cdot} \qquad\qquad 2.4$$

$$P_2^{\cdot} + M \xrightarrow{k_p} P_3^{\cdot} \qquad\qquad 2.5$$

$$P_3^{\cdot} + M \xrightarrow{k_p} P^{\cdot}_{(x+1)} \qquad\qquad 2.6$$
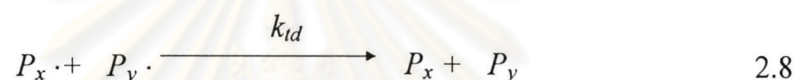
Growing chains can be terminated in one of two ways. Two growing chains can bump together and stick, their unshared electrons combining to form a single bond between them (combination):

$$P_x \cdot + P_y \cdot \xrightarrow{\quad k_{tc} \quad} P_{(x+y)} \qquad\qquad 2.7$$
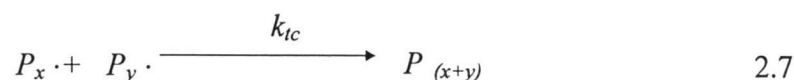
where $P_{(x+y)}$ is a dead polymer chain of (x+y) repeating units.

Or, one can abstract a hydrogen radical from the penultimate carbon of the other (disproportion)

$$P_x \cdot + P_y \cdot \xrightarrow{\quad k_{td} \quad} P_x + P_y \qquad\qquad 2.8$$

The relative proportion of each termination mode depends on the particular polymer and the reaction temperature, but in most cases, one or the other predominates.

2.3.1 Monomer concentration

The concentration of monomer in the reaction solution affects the properties of the resulting polymer, the kinetic of the reaction and the economics of the process. High monomer concentration results in increasing toughness of the intermediate gel polymer as the polymerization progresses. The toughness of the gel affects the design of equipment, the size of gel particles produced during agitation of the reaction mass and the method of heat removal. In addition, chain transfer to polymer increases with monomer concentration, especially at a high extent of conversion, and this results in increasing amounts of branching and self-crosslinking reactions that affect product

properties. Chain-transfer agents are useful to combat these side-reactions [17]. Another factor influencing the choice of monomer concentration is that the efficient use of the crosslinker increases with monomer concentration because the solubility of crosslinkers typically not very water soluble often increases with monomer concentration due to the increasing organic content of the monomer phase.

2.3.2 Initiators

The polymerization is initiated by a free radical in the aqueous phase, using thermally decomposable initiators, redox initiators or combinations. Redox systems used for the crosslinking copolymerization include couples of persulphate/bisulfite, persulphate/thiosulphate, persulphate/ascorbate and hydrogen peroxide/ascorbate. Thermal initiators include 2,2'-azobis-(2-amidinopropane)-dihydrochloride, persulphates, and 2,2'–azobis-(4-cyanopentanoic). Combinations of initiator are used when the polymerization takes place over a broad temperature range. In this case, it may be desirable to maintain a constant rate despite the change in the temperature. Appropriate concentration of multiple initiators can provide the desired constant rate of polymerization [18].

In graft copolymerization of vinyl monomers to polysaccharide substrates, initiation is accomplished using a redox reaction of an oxidant, such as the oxidized form of a metal ion, with oxidizable groups of the polysaccharide. When the metal ion is reacted with the graft substrate before the monomer is added, grafting efficiency is increased. In addition to initiating the polymerization reactions, initiators are a factor in reducing the levels of unreacted monomer during the drying step [19]. It can contribute to undesirable chain cleavage reactions to occur when the gel is handled at higher temperatures. For example, a higher content of soluble polymer is found when

sodium polyacrylate gels made by ammonium persulphate initiator are dried in a very hot oven [20].

2.3.3 Crosslinkers

2.3.3.1 Chemical crosslinking

The mechanism for most severely decreasing molecular freedom is chemical crosslinking which links the polymer chains together through covalent or ionic bonds to form a network. Occasionally the term curing is used to denote crosslinking. There are a number of ways crosslinking can be brought about, but basically they fall into two categories [21]:

1) crosslinking during polymerization by the use of polyfunctional monomer instead of difunctional monomers, and

2) crosslinking in a separate processing step after the linear (or branched) polymer is formed.

The crosslinks may contain the same structural features as the main chains, which is usually the case with the former, or they may have an entirely different structure, which is the unique characteristic of the latter. A number of extreme changes accompany crosslinking. If previously soluble, the polymer will no longer dissolve (except in the case of some ionically crosslinked polymers). In the presence of a solvent, a crosslinked polymer swells as solvent molecules penetrate the network. The degree of swelling depends on the affinity of solvent and polymer for one another, as well as on the level of crosslinking. It may be recalled that a solvent-swollen crosslinked polymer is called a gel. Covalently crosslinked polymer also loses their

flow properties. They may still undergo deformation, but the deformation will be reversible; that is, the polymer will exhibit elastic properties. Ionically crosslinked polymers will flow at elevated temperatures, however.

With network polymers, it is common to speak of the crosslink density, that is, the number of crosslinked monomer unites per main chain. The higher the crosslink density, the more rigid the polymer. Very high crosslink densities lead to embrittlement because crosslinking reduces segmental motion, it is frequently employed to increase the glass temperature.

2.3.3.2 Physical crosslinking

When polymer chemists use the term crosslinking, they invariably mean covalent chemical crosslinking. Once crosslinked, a polymer cannot be dissolved or molded. One approach has been to investigate thermally labile crosslinks, that is, chemical crosslinks that break apart on heating and reform on cooling. Ionic crosslinks fall into this category. The other approach has been to introduce strong secondary bonding attraction between polymer chains such that the polymer exhibits properties of a thermosetting material while remaining thermoplastic. Crystalline polymers fit into this category. Because of the very strong secondary forces rising from close chain packing, many of the mechanical and solution properties of crystalline polymers resemble those of crosslinked amorphous polymers. Certain materials intermolecularly associated through hydrogel bonds also behave like crosslinked polymers [21].

2.3.3.3 Crosslink density

One of the most important structure parameters characterizing crosslinked polymers is $\overline{M_c}$, the average molecular weight between crosslinks, which is directly related to the crosslink density. The magnitude of $\overline{M_c}$ significantly affects the physical and mechanical properties of crosslinked polymers and its determination has great practical significance. Equilibrium swelling is widely used to determine $\overline{M_c}$. Early research by Flory and Rehner laid the foundation for the analysis of equilibrium swelling. According to the theory of Flory and Rehner, the $\overline{M_c}$ for a perfect network can be written as in Equation 2.10 [22].

$$\overline{M_c} = -V_1\rho_p \frac{(\phi_p^{1-3} - \phi_p/2)}{[\text{In}(1-\phi_p) + \phi_p + \chi_{12}\phi_p^2]} \qquad 2.10$$

Where;

$\overline{M_c}$ is the number average molecular weight of the polymer between crosslinks,

V_1 is the molar volume of the solvent,

ρ_p is the polymer density,

ϕ_p is the volume fraction of polymer in the swollen gel, and

χ_{12} is the Flory-Huggins interaction parameter between solvent and polymer.

The swelling ratio, S, is equal to $1/\phi_p$. Here, the crosslink density, q, is defined as the mole fraction of crosslinked units,

$$q = \frac{M}{\overline{M_c}} \qquad\qquad 2.9$$

Where M is the molecular weight of polymer repeat unit. We defined q in Equation 2.9 in order to simplify a direct comparison with the mole fraction of divinyl monomers in copolymerization.

2.4 Specific polymerization techniques

Commercial superabsorbent polymers are prepared using a large variety of techniques, but they can be grouped into five general categories:

2.4.1 Solution polymerization

The polymerization of acrylic acid or sodium acrylate with a crosslinking agent in aqueous solution would seem to be a straightforward process. The monomer and crosslinking agent are dissolved in water at a desired concentration, usually from about 10-70%, since polymerization of undiluted acrylic acid is extremely dangerous due to the high heat of polymerization and rapid polymerization kinetics. The monomer solution is deoxygenated by bubbling an inert gas through the solution, or by a series of evacuations and repressurizations with an inert gas, the desired free radical initiator is added and the temperature is bought to the appropriate point for

polymerization to begin. However, the use of this technique in industrial practice is complicated by a variety of factors, the solution to which is the subject of numerous patents.

2.4.2 Graft polymerization

Water soluble polymers such as starch and poly(vinyl alcohol) are grafted into superabsorbents in order to modify the properties. A certain process benefits from increased viscosity of the monomer solution, and the water soluble, graft substances can serve this purpose [23, 24]. Historically, the "superslurper" absorbents were made from acrylonitrile grafts to starch, and the currently used acrylic acid grafts to starch appear to have developed from the earlier work. Special initiators are useful to increase grafting efficiency with polymers containing hydroxyl sites. Metal ions, such as cerium, complex with the hydroxyl sites and serve as a locus for the nascent free radical formed by oxidation of the substrate. For example, starch has been reacted with a partially neutralized acrylic acid and a diacrylate ester crosslinking agent, using Ce^{4+} as a free radical initiator. The gel like reaction product was dried and pulverized [25]. Graft copolymers can also be prepared using an inverse suspension polymerization [26].

2.4.3 Crosslinking after polymerization

In this technique, the polyacrylate is formed in first step, as a soluble polymer, which is then reacted in a second step with a suitable crosslinking agent. These are any of a hung variety of compounds which can react with carboxylic groups including amines, alcohols, epoxides and polyvalent metal ions. A benefit of this technology is that the absorbent polymer can be formed in to a desired shape by

mixing the soluble polymer and crosslinking agent and curing in place, for example onto fibers on the surface of a sheet of tissue. Drawbacks to this technology are the handing of the viscous solutions of polymer and they are through mixing with the crosslinking agent and any catalysis required [27].

2.4.4 Suspension polymerization

Suspension polymerization is a system in which monomer are suspended as the discontinuous phase of droplets in a continuous phase and polymerized. The reactor product is slurry of suspended polymer particles. The monomer suitable for suspension polymerization usually can be polymerized by free radical mechanism. The continuous phase is usually water, as most monomer is relatively insoluble in water. The terms pearl polymerization and bead polymerization describe the smooth, spherical particles from some suspension polymerization.

2.4.5 Inverse suspension polymerization

Inverse suspension polymerization, which recently has attained commercial importance, beginning with a concentrated aqueous solution of monomers dispersed in hydrophobic organic solvents. The technique is particularly useful with acrylamide, methacrylamide, acrylic acid, methacrylic acid, salts of the corresponding acids, and quaternary ammonium monomers such as quaternized diethylaminoethyl methacylate and vinylbenzyl trimethylammonium chloride and their mixtures. Generally 50-80% monomer in a concentrated solution with water is dispersed along with water soluble initiator such as persulphates, hydrogen peroxide, and redox activators. For external phases, one may use aliphatic hydrocarbons or less frequently toluene, xylene or

chlorinated phases one may use aliphatic hydrocarbons or less frequently toluene, xylene or chlorinated hydrocarbons [28]. This system is different from suspension polymerization in a phase of monomer solution, solubility of initiator in an organic phase and aqueous phase.

2.5 Silicon dioxide (silica)

2.5.1 Types and methods of manufacture

In order to obtain extremely fine particle silica, chemical synthesis is necessary. A form of natural silica, usually silica sand, is the raw material. In one process, this is converted to a soluble silicate by fusion with an alkali. The silicate, in water solution, is then reconverted to hydrated silica by the addition of an acid. The conditions of this precipitation are carefully controlled to produce uniform particles of silica. The product is filtered, washed and dried. Several precipitated silica grades having an average particle size of 20 to 100 nm (0.02 to 0.1 μm) are produced [29].

The pyrogenic silicas are produced by a much more complex method. Silicon tetrachloride, prepared from sand, chlorine and carbon, is reacted at high temperature in a hydrogen and oxygen flame. The product is an ultrapure, fine particle size anhydrous silica. The average particle size in several grades ranges from 7 to 50 nm (0.007 to 0.05 μm).

The hydrogels and aerogels are also precipitated silicas, but are finished in a different manner. The aerogels are dried above the critical temperature, under pressure, to prevent collapse of the gel-like structure. They remain particulate in structure.

The silica gels are manufactured similarly, except the precipitated gel is allowed to set-up, then washed, dried and ground. There are no ultimate particles, as such, but only aggregates of gel. These aggregates are 4-20 μm in size and are highly porous.

2.5.2 Physical and chemical properties

A summary of pertinent physical properties of the synthetic silicas is given in Table 2.4. They are characterized by very high specific surface area and high oil absorption. The particulate silicas (all but the hydrogels) have extremely small particles which are approximately spherical and reasonably nonporous. The particles are fused into aggregates of a few to perhaps a hundred particles. The hydrogels, on the other hand are composed entirely of very large aggregates (4-20 μm) which can be considered a network of particles.

The other major distinction among the synthetic silicas is the water adsorption. This is attributed to the silanol content on the surface. The precipitated varieties, including the aerogels and hydrogels, have a fully hydroxylated surface, leading to relatively high water adsorption compared to the naturally occurring silicas. The pyrogenic silicas have only a partially hydroxylated surface, roughly one-quarter that of precipitated silica. Some silicas are subsequently modified (by heat treatment or surface coating) to reduce water adsorption.

All of the synthetic silicas can be modified with organofunctional silanes. These can be used to increase the compatibility with the plastic system, often giving improved adhesion, reduced water adsorption, and increased strength.

Table 2.4 Typical properties of silica fillers [29].

	Average Particle Size, μm[a]	Sp. Surface Area, m²/g	Oil Absorption, g/100g	"Free" Moisture, %
I. Natural silicas				
A. Quartz				
Powdered	1.5 - 10	0.2 – 2.1	24 – 36	0.05
Cryptocrystalline	2 – 10	1 – 1.4	29 – 31	0.025
Microcrystalline	4	2	20	0.01
B. Diatomaceous				
Natural	3 – 12	15	150	4
Calcined	3 – 12	3	90 –140	0.5
II. Synthetic				
A. Precipitated	0.02 – 0.1	45 – 150	110 – 160	5
B. Pyrogenic	0.007 – 0.05	50 – 390	280	1
C. Aerogels	0.01 – 0.02	130 – 320	260 – 350	3
D. Hydrogels	(4 – 20)[b]	220 – 700	90 -250	2 - 10

a. Several products of different average size account for ranges used.

b. Aggregate size, not particulate.

2.6 Literature survey

Recent researches on the synthesis of superabsorbent polymer and important physical property development are listed as below:

Liu and Rempel [30] prepared the high water-absorbent copolymer comprising acrylic acid and acrylamide in the presence of a crosslinking agent, monofunctional aldehyde, by a solution polymerization technique via a potassium

metabisulfite redox initiation system. The copolymer formed absorbed about 900 g water/g dry copolymer. They found that the absorption behavior of the superabsorbents related to their chemical composition and the nature of the solvent.

Rangaraj *et al.*, [31] synthesized homopolymers and copolymers of acrylamide and acrylic acid by the free radical solution polymerization technique using hydrogen peroxide, potassium persulfate, and benzoyl peroxide as initiators. The copolymers were purified by removing homopolymers. The homopolymers and copolymers were characterized by infrared (IR), ^{13}C-nuclear magnetic resonance (NMR), ^{1}H-NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and viscosity measurements.

Dubrovskii, *et al.*, [32] synthesized superabsorbent hydrogels (SAHs) by methylenebisacrylamide or by γ-radiation crosslinking of the high molecular AM-AA coplymer in aqueous solution. The polymerization was initiated with ammonium persulphate: tetramethylethylenediamine (2:1) in 20% aqueous solution of the monomer at 45°C. The modified swelling theory had been used to develop a system of experimental and computational methods for the evaluation of supergel network parameter.

Yao and Zhou [33] prepared a series of novel copolymer superabsorbents based on acrylamide, sodium allylsulfonate, sodium acrylate, and *N,N'*-methylenebisacrylamide at a copolymerization temperature at 35°C. The resulting superabsorbents had a fast swelling rate. The absorbency increased to maximum, 437 times its dry copolymer weight as the crosslinking agent concentration increased, 5×10^{-3} mol dm^{-3}, but an excess of crosslinking agent led to a decrease swelling. Their water retention was observed under the pressures of 1-10 kg cm^{-3} and temperatures at 60°C and 100°C, respectively. The water retention of soil had been enhanced using the

poly(acrylamide-*co*-sodium allylsulfonate-*co*-sodium acrylate) superabsorbent; its use is for an enhancement of bean growth.

Smith and Lind [34] improved absorption under pressure and fast absorption rate properties of superabsorbent polymer which was obtained by polymerizing a solution containing carboxylic acid monomers or water soluble salts, and a crosslinking agent. The most preferred crosslinking agents were bis-acrylamide such as *N,N'*-methylenebisacrylamide, the di-, tri- or polyesters of unsaturated mono or polycarboxylic acid polyols, such as trimethylolpropane triacrylate, the di- or tri-glycidyl ethers of polyols such as ethyleneglycol diglycidyl ether, the multi-substituted allyl amines such as diallyl amine and triallyl amine, or their mixtures. A preferred carbonate blowing agents were $MgCO_3$, $(NH_4)_2CO_3$, Na_2CO_3, and their mixture and a polymerization initiator are added, individually or in combination, to the solution to form a carbonated monomer solution. A polymerization initiator was then added to the carbonated monomer solution which was then polymerized at the temperature ranging from about 0^oC to 130^oC, forming a microcellular hydrogel. The hydrogel was ground into gel pieces and dried at temperature ranging from about 85^oC to 210^oC. Mixture was formed from 100 parts by weight of the polymer and about 0.001 to 30 parts by weight of a crosslinking agent. The polymer was reacted with the crosslinking agent to crosslinking molecular chains existing on surface of the polymer, forming the superabsorbent polymer.

Chen *et al.*, [35] synthesized superporous hydrogels based on monomers: acrylic acid (AA), acrylamide (AM), *N*-isopropyl acrylamide (NIPAM), vinylpyrrolidone (VP), hydroxyethylmethacrylate (HEMA), potassium salt of 3-sulfopropyl acrylate (SPAK), 2-acrylamide-2-methyl-1-propanesulfonic acid (AMPS), 2-(acryloxyethyl) trimethyl ammonium methylsulfate (ATMS) and hydroxypropyl methacrylate (HPMA), or *N,N'*-methylenebisacrylamide (N-MBA) as a crosslinking

agent, ammonium persulfate (APS) and *N,N,N',N'-t*etramethylethylenediamine (TEMED) as a coinitiator and Pluronic F127 (PF127) as a foam stabilizer, crosslinking polymerization of monomer in a test tube (20 mm outer diameter x 150 mm in length) and presence of carbon dioxide gas bubbles, which were generated by a reaction of sodium bicarbonate with an acid. The use of the $NaHCO_3$/acid system allowed easy control of timing for gelation and foam formation. The PF127 was the best foam stabilizer for most of the monomer systems. The resulting superabsorbents gave a fast swelling rate. The swelling ratio (Q) is 368 ± 34 times its dry copolymer weight. The average diameter of the pores of superporous hydrogels is approximately 150 μm, and some pores are as large as 300 μm.

Zhou *et al.*, [36] synthesized hydorgels of acrylamide (AM), sodium methallylsufonate (MSAS), sodium acrylate, and *N,N'*-methylenebisacrylamide (BisA) in aqueous solution using 1.33×10^{-3} mol dm^{-3} potassium persulfate (KPS)/3.0×10^{-3} mol dm^{-3} of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as the redox initiator. These gels absorbed about 125 times their own weight in distilled water, and 21 times in 0.9%NaCl solution. Conversion and absorbency increase with the MSAS concentration. Further increase of the MSAS concentration leads to a decrease in absorbency.

Karadag *et al.*, [37] have reported that the acrylamide/itaconic acid (AM/IA) hydrogels were prepared by irradiating with γ-radiation used in experiments on the uptake of some cationic dyes such as basic red 5 (BR-5), basic violet 3 (BV-3) and brilliant cresyl blue (BCB). The removal of the cationic dyes to AM/IA hydrogels is studied by batch adsorption technique. In the experiments of the adsorption, L3 type (Langmiur) adsorption in Giles classification system was found. Adsorption studies indicated that monolayer coverages of AM/IA hydrogel by these dyes were increased with the following order: BCB>BR-5>BV-3.

Chen and Zhao [38] prepared polyacrylate superabsorbent by *in situ* aqueous solution polymerization in a polyethylene bag, which was submerged in a $70^{\circ}C$ water bath. The monomer mixture was polymerized *in situ* for 2 h and a polymeric gel was the formed Using potassium persulfate (KPS) as an initiator and triethylene glycol diacrylate (TEGDA) as a crosslinking agent, the water absorbency increase linearly with increases of the initiator content. The water absorbency is changed slightly when the bath temperature is between $50^{\circ}C$ and $60^{\circ}C$ and water absorbency increases continuously when the bath temperature is between $60^{\circ}C$ and $80^{\circ}C$. Water absorbency increased linearly with increase of the content of a chain-transfer agent of isopropanol.

Wu *et al.*, [39] studied a novel starch-graft-acrylamide/mineral powder superabsorbent composite with water about 4000 times is synthesized by graft-copolymerization reaction among acrylamide, potato starch and mineral ultrafine powder, followed by hydrolysis with sodium hydroxide. It is found that the composites doped with kaolinite powder posses higher water absorbency than those doped with bentonite or sercite powder, since the kaolinite powder can moderately disperse in the water and crosslink with acrylamide and starch. By controlling the amount of NaOH and reaction time during saponification process, the hydrophilic group on the composites can be adjusted, it is found that the collaborative absorbent effect of $-CONH_2$, $-COONa$ and $-COOH$ groups is superior to that of single $-CONH_2$, $-COONa$ and $-COOH$ group. By the IR characterization, the polymerization reaction mechanism and structure of the composites is supposed, the mineral ultrafine powder as a crosslinking point play an important role in the formation of network structure superabsorbent composites.

Kourosh and Zohuriaan-Mehr [40] Superabsorbent hydrogel composites (SHCs) were prepared through an optimized rapid solution polymerization of concentrated partially neutralized acrylic acid in the presence of a crosslinking agent

under normal atmospheric conditions. Kaolin was used as an inorganic component in the polymerization process to strengthen the hydrogel products. Compared with the kaolin-free hydrogel (control), kaolin caused a reduced equilibrium swelling and swelling rate as low as 17-31% and 19-29%, respectively. Kaolin, however, resulted in enhanced gel strength as high as 21-35% compared to the control.

Chen and Park [41] synthesized superporous hydrogels which swell fast with high swelling ratios for development of gastric retention devices. The mechanical strength of superporous hydrogels was substantially increased by making superporous hydrogel composites. The composite materials used were hydrophilic particulate materials commonly used as disintegrants in pharmaceutical tablets. Ac-Di-Sol was used as a model composite material. Addition of Ac-Di-Sol resulted in significant improvement in the properties of superporous hydrogels. SEM examination showed that the composites material increased the physical crosslinking density that provided high strength and prevented polymer chains from collapsing during air drying. The superporous hydrogel composites possess properties suitable for gastric retention.

Gao and Heimann [5] synthesized superabsorbent poly(acrylamide)-montmorillonite composite (SAPC). The structure of SAPC was studied by means of XRD, SEM, NMR, FTIR, TGA and DSC. The study showed that the acrylamide was intercalated in the lamina of clay in bimolecular layers. Viscoelastic superabsorbent PAM/montmorillonite composite (SAPC) material with a potential water absorption capacity, Q in excess of 2,000 g water/g SAPC shows chemomechanical behavior when subjected to an electric filed in solutions of different ionic content. The material's swelling ratio is a strong function of the ionic strength as well as the pH of the solution to be absorbed.